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(54) ELECTRODE AND LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To prevent deterioration in capacity in charging/discharging cycles by using a material obtained by replacing part of Mn of spinel lithium manganese oxide with B and/or Al, or B and/or Al and a transition metal.

SOLUTION: An electrode, especially a positive electrode of a lithium secondary battery is constituted with a material prepared by replacing part of Mn of spinel lithium manganese oxide with boron and/or aluminum, or boron and/or aluminum and a transition metal, especially with a material represented by $LiB_xMyMn_{2-x-y}O_2$ ($0 < x, 0 \leq y, 0 < x+y < 1$, M is at least one metal selected from the group comprising Cr, Fe, Co, and Ni), or $LiAl_xMyMn_{2-x-y}O_2$ ($0 < x, 0 \leq y, 0 < x+y < 1$, M is at least one metal selected from the group comprising Cr, Fe, Co, and Ni). And especially x is 0.01-1, y is 0.01-1, and x+y is 0.01-1.

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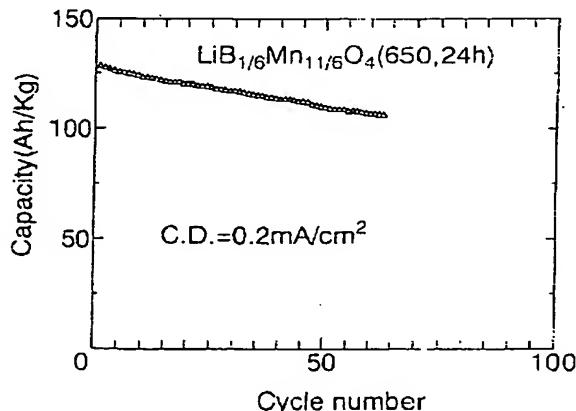
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(54)【発明の名称】電極、及びリチウム二次電池

(57)【要約】

【課題】充・放電サイクルを繰り返した際の容量劣化が防止されたリチウム二次電池を提供することである。

【解決手段】スピネル型リチウムマンガン酸化物のマンガンの一部をホウ素及び/又はアルミニウム、あるいはホウ素及び/又はアルミニウムと遷移金属とで置換された材料を用いて構成されてなる電極。



〔特許請求の範囲〕

〔請求項1〕スピネル型リチウムマンガン酸化物のマンガンの一部をホウ素及び/又はアルミニウム、あるいはホウ素及び/又はアルミニウムと遷移金属とで置換された材料を用いて構成されてなることを特徴とする電極。

〔請求項2〕 $LiB_xM_yMn_{2-x-y}O_4$ ($0 < x, 0 \leq y, 0 < x+y < 1$, MはCr, Fe, Co, Niの群の中から選ばれる少なくとも一種) で表される材料を用いて構成されてなることを特徴とする電極。

〔請求項3〕 $LiAl_xM_yMn_{2-x-y}O_4$ ($0 < x, 0 \leq y, 0 < x+y < 1$, MはCr, Fe, Co, Niの群の中から選ばれる少なくとも一種) で表される材料を用いて構成されてなることを特徴とする電極。

〔請求項4〕 x は0.01~1, y は0~1, $x+y$ は0.01~1であることを特徴とする請求項2又は請求項3の電極。

〔請求項5〕請求項1~請求項4いずれかの電極からなる正極と、負極と、電解液とからなることを特徴とするリチウム二次電池。

〔請求項6〕負極がインターカレーション化合物の群の中から選ばれる材料で構成されたものであることを特徴とする請求項5のリチウム二次電池。

〔請求項7〕電解液がリチウム塩を有機溶媒に溶解した非水系電解液であることを特徴とする請求項5のリチウム二次電池。

〔発明の詳細な説明〕

〔0001〕

〔発明の属する技術分野〕本発明はリチウム二次電池に関する。

〔0002〕

〔発明が解決しようとする課題〕Thackerayらにより $LiMn_2O_4$ が4Vと言う高電位を示すリチウム二次電池用の正極材料としての可能性が示唆されて以来、多くの研究者により盛んに研究されている。しかし、 $LiMn_2O_4$ を正極として用いたリチウム二次電池は、充・放電を繰り返すと、徐々に容量が低下する欠点がある。

〔0003〕すなわち、 $LiMn_2O_4$ からLiを離脱させると、リチウム組成が1/2付近で電位の屈曲が起き、同時に格子体積が大きく収縮する。逆に、リチウム組成が小さい領域からリチウムを挿入していくと、リチウム組成が1/2付近で格子体積の膨張が起きる。このように充・放電時に格子体積の膨張・収縮を伴った相転移が起こり、このことが充・放電サイクルを繰り返した際の容量劣化の原因と考えられる。

〔0004〕この充・放電サイクルの繰り返しによる容量劣化を改善する為、 $LiMn_2O_4$ のMnの一部を他の金属イオンで置換した $Li[M_xMn_{2-x}]O_4$ (MはCr, Co, Ni, Ti, Fe, Mg, Ba, Zn,

Ge, Nb) やリチウムイオンで置換した $Li[Li_xMn_{2-x}]O_4$ が試みられた。そして、例えば $LiCr_xMn_{2-x}O_4$ はスピネルの母構造の安定性が増し、サイクル特性が向上した。

〔0005〕しかし、更なる改善が求められた。従って、本発明が解決しようとする課題は、充・放電サイクルを繰り返した際の容量劣化が防止されたリチウム二次電池を提供することである。

〔0006〕

10 〔課題を解決するための手段〕前記本発明の課題は、スピネル型リチウムマンガン酸化物のマンガンの一部をホウ素及び/又はアルミニウム、あるいはホウ素及び/又はアルミニウムと遷移金属とで置換された材料を用いて構成されてなることを特徴とする電極によって解決される。

〔0007〕特に、 $LiB_xM_yMn_{2-x-y}O_4$ ($0 < x, 0 \leq y, 0 < x+y < 1$, MはCr, Fe, Co, Niの群の中から選ばれる少なくとも一種) で表される材料を用いて構成されてなることを特徴とする電極によ

20 って解決される。又、 $LiAl_xM_yMn_{2-x-y}O_4$ ($0 < x, 0 \leq y, 0 < x+y < 1$, MはCr, Fe, Co, Niの群の中から選ばれる少なくとも一種) で表される材料を用いて構成されてなることを特徴とする電極によって解決される。

〔0008〕尚、上記 $LiB_xM_yMn_{2-x-y}O_4$ や $LiAl_xM_yMn_{2-x-y}O_4$ において、 x は0.01~1, y は0~1, $x+y$ は0.01~1であるものが好ましい。特に、 x は0.05~0.2が好ましい。 y は0.05~0.2が好ましい。又、前記本発明の課題

30 は、上記の電極からなる正極と、負極と、電解液とからなることを特徴とするリチウム二次電池によって解決される。

〔0009〕尚、上記リチウム二次電池における負極は、例えばリチウム金属や炭素のようなインターカレーション化合物の群の中から選ばれる材料で構成される。又、上記リチウム二次電池における電解液はリチウム塩を有機溶媒に溶解した非水系電解液で構成される。そして、上記のように構成させた電極は、スピネル型リチウムマンガン酸化物のマンガンの一部を、Mnより原子量が小さく、酸素との結合エネルギーが強い三価のホウ素イオンやアルミニウムイオンで置換した構造のものであるから、充・放電サイクルを繰り返した際の容量劣化が効果的に防止される。

〔0010〕

〔発明の実施の形態〕本発明の電極、特にリチウム二次電池の正極は、スピネル型リチウムマンガン酸化物のマンガンの一部をホウ素及び/又はアルミニウム、あるいはホウ素及び/又はアルミニウムと遷移金属とで置換された材料を用いて構成される。特に、 $LiB_xM_yMn_{2-x-y}O_4$ ($0 < x, 0 \leq y, 0 < x+y < 1$, MはCr, Fe, Co, Ni, Ti, Fe, Mg, Ba, Zn,

r, Fe, Co, Niの群の中から選ばれる少なくとも一種)で表される材料を用いて構成される。又、 $LiAl_xMn_{2-x}O_y$ ($0 < x, 0 \leq y, 0 < x+y < 1$, MはCr, Fe, Co, Niの群の中から選ばれる少なくとも一種)で表される材料を用いて構成される。そして、特に、xは0.01~1(特に、0.05~0.2), yは0.01~1(特に、0.05~0.2), $x+y$ は0.01~1である。

【0011】又、本発明のリチウム二次電池は、上記の電極からなる正極と、負極と、電解液とからなる。このリチウム二次電池における負極は、例えばリチウム金属や炭素のようなインターカレーション化合物の群の中から選ばれる。又、電解液はリチウム塩有機溶媒に溶解した非水系電解液で構成される。以下、更に説明する。

【0012】 $[LiB_xMn_{2-x}O_y]$

炭酸リチウム、水酸化リチウム等のリチウム塩；炭酸マンガン、酢酸マンガン、ショウ酸マンガン、水酸化マンガン、二酸化マンガン等のマンガン塩あるいはオキシ水酸化マンガンやマンガン酸化物；ホウ酸、二酸化ホウ素等のホウ素塩あるいはホウ素酸化物を、 $Li : B : Mn = 1 : x : 2 - x$ (元素比)となるよう秤量する。

【0013】秤量した原料をメノウ乳鉢で充分に混合する。混合後、空気中あるいは酸素気流中にて450°Cで90分間かけて熱処理する。この後、メノウ乳鉢で粉碎し、再度、600~800°Cで24時間かけて焼成し、そして徐冷し、 $LiB_xMn_{2-x}O_y$ を得た。

$[LiB_xMn_{2-x}O_y]$ (MはCr, Fe, Co, Ni)

炭酸リチウム、水酸化リチウム等のリチウム塩；炭酸マンガン、酢酸マンガン、ショウ酸マンガン、水酸化マンガン、二酸化マンガン等のマンガン塩あるいはオキシ水酸化マンガンやマンガン酸化物；ホウ酸、二酸化ホウ素等のホウ素塩あるいはホウ素酸化物；M (MはCr, Fe, Co, Ni) の炭酸塩、酢酸塩、ショウ酸塩などの塩、酸化物、水酸化物あるいはオキシ水酸化物などの化合物を、 $Li : B : M : Mn = 1 : x : y : 2 - x - y$ (元素比)となるよう秤量する。

【0014】秤量した原料をメノウ乳鉢で充分に混合する。混合後、空気中あるいは酸素気流中にて450°Cで90分間かけて熱処理する。この後、メノウ乳鉢で粉碎し、再度、600~800°Cで24時間かけて焼成し、そして徐冷し、 $LiB_xMn_{2-x}O_y$ (MはCr, Fe, Co, Ni)を得た。

【0015】 $[LiAl_xMn_{2-x}O_y]$

炭酸リチウム、水酸化リチウム等のリチウム塩；炭酸マンガン、酢酸マンガン、ショウ酸マンガン、水酸化マンガン、二酸化マンガン等のマンガン塩あるいはオキシ水酸化マンガンやマンガン酸化物；水酸化アルミニウム等のアルミニウム化合物を、 $Li : Al : Mn = 1 : x : 2 - x$ (元素比)となるよう秤量する。

【0016】秤量した原料をメノウ乳鉢で充分に混合する。混合後、空気中あるいは酸素気流中にて450°Cで90分間かけて熱処理する。この後、メノウ乳鉢で粉碎し、再度、600~800°Cで24時間かけて焼成し、そして徐冷し、 $LiAl_xMn_{2-x}O_y$ を得た。

$[LiAl_xMn_{2-x}O_y]$ (MはCr, Fe, Co, Ni)

炭酸リチウム、水酸化リチウム等のリチウム塩；炭酸マンガン、酢酸マンガン、ショウ酸マンガン、水酸化マンガン、二酸化マンガン等のマンガン塩あるいはオキシ水酸化マンガンやマンガン酸化物；水酸化アルミニウム等のアルミニウム化合物；M (MはCr, Fe, Co, Ni) の炭酸塩、酢酸塩、ショウ酸塩などの塩、酸化物、水酸化物あるいはオキシ水酸化物などの化合物を、 $Li : Al : M : Mn = 1 : x : y : 2 - x - y$ (元素比)となるよう秤量する。

【0017】秤量した原料をメノウ乳鉢で充分に混合する。混合後、空気中あるいは酸素気流中にて450°Cで90分間かけて熱処理する。この後、メノウ乳鉢で粉碎し、再度、600~800°Cで24時間かけて焼成し、そして徐冷し、 $LiAl_xMn_{2-x}O_y$ (MはCr, Fe, Co, Ni)を得た。

【0018】上記のようにして得た材料とアセチレンブラック等の集電材及びポリテトラフルオロエチレン等のバインダをメノウ乳鉢で混練し、フィルム状に圧延し、円形に打ち抜いて電極ペレットとした。そして、この電極ペレットからなる正極、例えばリチウム金属や炭素のようなインターカレーション化合物の群の中から選ばれる材料で構成された電極からなる負極、リチウム塩有機溶媒に溶解した非水系電解液で構成される電解液とを用いてリチウム二次電池を構成した。

【0019】

【実施例1】上記発明の実施の形態で説明したようにして $LiB_{1/2}Mn_{11/6}O_4$ を得、これを用いて正極を構成し、金属リチウムを用いて負極を構成し、1mol/1の過塩素酸リチウムの炭酸プロピレン溶液で電解液を構成し、これらによりリチウム二次電池を構成した。

【0020】

【実施例2】上記発明の実施の形態で説明したようにして $LiAl_{1/6}Mn_{11/6}O_4$ を得、これを用いて正極を構成し、金属リチウムを用いて負極を構成し、1mol/1の過塩素酸リチウムの炭酸プロピレン溶液で電解液を構成し、これらによりリチウム二次電池を構成した。

【0021】そして、電流密度0.2mA/cm²で4.5vから3.5vの電位範囲で充・放電試験を行い、放電時の容量密度の変化を調べたので、その結果を図2に示す。

【0022】

【実施例3】上記発明の実施の形態で説明したようにして $LiB_{1/12}Cr_{1/12}Mn_{11/6}O_4$ を得、これを用いて

正極を構成し、金属リチウムを用いて負極を構成し、1 mol/lの過塩素酸リチウムの炭酸プロピレン溶液で電解液を構成し、これらによりリチウム二次電池を構成した。

【0023】そして、電流密度0.2mA/cm²で4.5Vから3.5Vの電位範囲で充・放電試験を行い、放電時の容量密度の変化を調べたので、その結果を図3に示す。

【0024】

【実施例4】上記発明の実施の形態で説明したようにしてLiB_{1/2}Fe_{1/2}Mn_{1/6}O₄を得、これを用いて正極を構成し、金属リチウムを用いて負極を構成し、1 mol/lの過塩素酸リチウムの炭酸プロピレン溶液で電解液を構成し、これらによりリチウム二次電池を構成した。

【0025】

【実施例5】上記発明の実施の形態で説明したようにしてLiB_{1/2}Co_{1/2}Mn_{1/6}O₄を得、これを用いて正極を構成し、金属リチウムを用いて負極を構成し、1 mol/lの過塩素酸リチウムの炭酸プロピレン溶液で電解液を構成し、これらによりリチウム二次電池を構成した。

【0026】

【実施例6】上記発明の実施の形態で説明したようにしてLiB_{1/2}Ni_{1/2}Mn_{1/6}O₄を得、これを用いて正極を構成し、金属リチウムを用いて負極を構成し、1 mol/lの過塩素酸リチウムの炭酸プロピレン溶液で電解液を構成し、これらによりリチウム二次電池を構成した。

【0027】

【実施例7】上記発明の実施の形態で説明したようにしてLiAl_{1/2}Cr_{1/2}Mn_{1/6}O₄を得、これを用いて正極を構成し、金属リチウムを用いて負極を構成し、1 mol/lの過塩素酸リチウムの炭酸プロピレン溶液で電解液を構成し、これらによりリチウム二次電池を構成した。

【0028】

【実施例8】上記発明の実施の形態で説明したようにしてLiAl_{1/2}Fe_{1/2}Mn_{1/6}O₄を得、これを用いて正極を構成し、金属リチウムを用いて負極を構成し、1 mol/lの過塩素酸リチウムの炭酸プロピレン溶液で電解液を構成し、これらによりリチウム二次電池を構成した。

【0029】

【実施例9】上記発明の実施の形態で説明したようにしてLiAl_{1/2}Co_{1/2}Mn_{1/6}O₄を得、これを用いて正極を構成し、金属リチウムを用いて負極を構成し、1 mol/lの過塩素酸リチウムの炭酸プロピレン溶液で電解液を構成し、これらによりリチウム二次電池を構成した。

【0030】

【実施例10】上記発明の実施の形態で説明したようにしてLiAl_{1/2}Ni_{1/2}Mn_{1/6}O₄を得、これを用いて正極を構成し、金属リチウムを用いて負極を構成し、1 mol/lの過塩素酸リチウムの炭酸プロピレン溶液で電解液を構成し、これらによりリチウム二次電池を構成した。

【0031】

【特性】上記各例のリチウム二次電池について、電流密度0.2mA/cm²で4.5Vから3.5Vの電位範囲で充・放電試験を行い、放電時の容量密度の変化を調べたので、幾つかを図1(実施例1)、図2(実施例2)、図3(実施例3)に示す。

【0032】これによれば、充・放電サイクルを繰り返した際の容量劣化が防止されていることが判る。特に、スピネル型リチウムマンガン酸化物のマンガンの一部をホウ素及び/又はアルミニウムと遷移金属とで置換された材料LiB_xM_yMn_{2-x-y}O₄(0 < x, 0 < y, 0 < x+y < 1, MはCr, Fe, Co, Niの群の中から選ばれる少なくとも一種)やLiAl_xM_yMn_{2-x-y}O₄(0 < x, 0 < y, 0 < x+y < 1, MはCr, Fe, Co, Niの群の中から選ばれる少なくとも一種)で表される材料を用いて構成されてなる電極のものは、充・放電サイクルを繰り返した際の容量劣化が防止されていることが判る。

【0033】

【発明の効果】充・放電サイクルを繰り返した際の容量劣化が防止される。

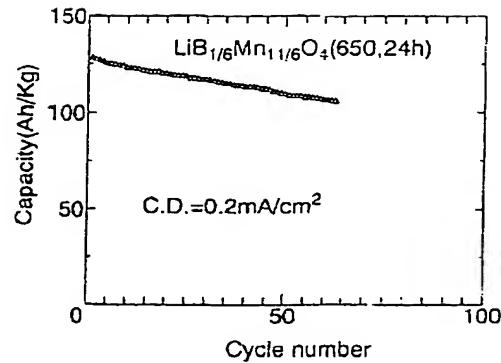
【図面の簡単な説明】

【図1】実施例1のリチウム二次電池の放電時の容量密度の変化を示すグラフ

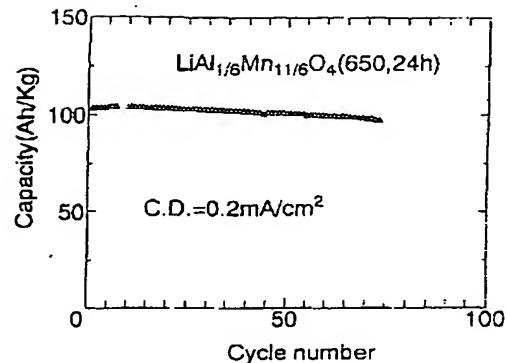
【図2】実施例2のリチウム二次電池の放電時の容量密度の変化を示すグラフ

【図3】実施例3のリチウム二次電池の放電時の容量密度の変化を示すグラフ

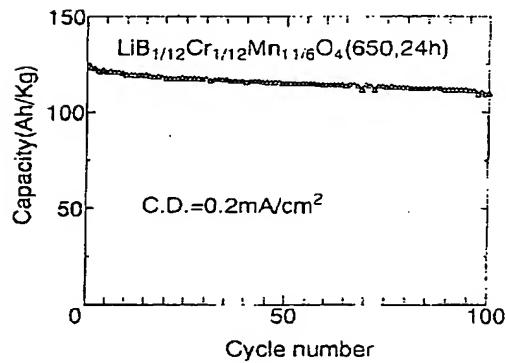
【図1】



【図2】



【図3】



JAPANESE

[JP,09-270259,A]

AE

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD EFFECT OF THE INVENTION TECHNICAL
PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] The electrode which is constituted using the material replaced by boron and/or aluminum or boron and/or aluminum, and transition metals in some manganese of a spinel type lithium manganic acid ghost, and is characterized by the bird clapper.

[Claim 2] The electrode which is constituted using the material expressed with $LiB_x M_y Mn_{2-x-y} O_4$ ($0 < x, 0 \leq y, 0 < x+y < 1$ and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind), and is characterized by the bird clapper.

[Claim 3] The electrode which is constituted using the material expressed with $LiAl_x M_y Mn_{2-x-y} O_4$ ($0 < x, 0 \leq y, 0 < x+y < 1$ and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind), and is characterized by the bird clapper.

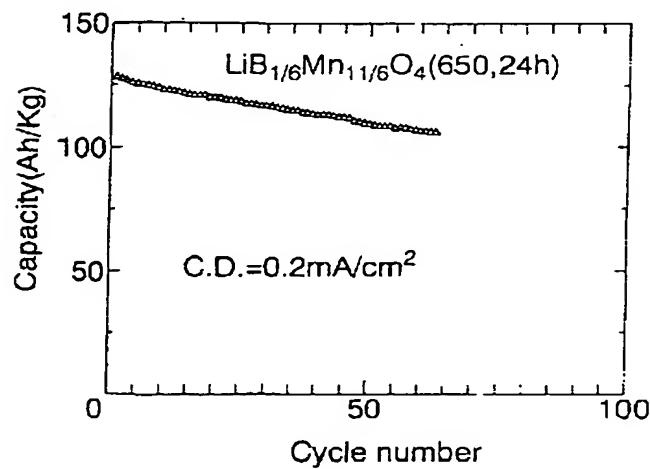
[Claim 4] For $0.01-1y$, x is [0-1, and $x+y$] the electrode of the claim 2 characterized by being 0.01-1, or a claim 3.

[Claim 5] a claim 1 - a claim 4 -- the lithium secondary battery characterized by the bird clapper from the positive electrode which consists of one of electrodes, a negative electrode, and the electrolytic solution

[Claim 6] The lithium secondary battery of the claim 5 characterized by a negative electrode consisting of material chosen from the groups of an intercalation compound.

[Claim 7] The lithium secondary battery of the claim 5 characterized by being the nonaqueous electrolyte by which the electrolytic solution dissolved lithium salt in the organic solvent.

[Translation done.]

Drawing selection [Representative drawing] 

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to a lithium secondary battery.

[0002]

[Problem(s) to be Solved by the Invention] It is LiMn₂O₄ by Thackeray and others. Since the possibility as a positive-electrode material for lithium secondary batteries which shows the high potential called 4v was suggested, many researchers have inquired briskly. However, LiMn₂O₄ The lithium secondary battery used as a positive electrode has the fault to which capacity falls gradually, when charge and discharge are repeated.

[0003] Namely, LiMn₂O₄ If a shell Li is made to break away, incursion of potential will occur [lithium composition] in the 1/2 neighborhood, and grid volume will contract greatly simultaneously. On the contrary, if lithium composition inserts a lithium and goes from a small field, expansion of grid volume will occur [lithium composition] in the 1/2 neighborhood. Thus, the phase transition accompanied by expansion and contraction of grid volume happens at the time of charge and discharge, and it is considered the cause of capacity degradation at the time of this repeating a charge-and-discharge cycle.

[0004] In order to improve capacity degradation by the repeat of this charge-and-discharge cycle, it is LiMn₂O₄. Li_{[Mx Mn_{2-x}] O₄} (M is Cr, Co, nickel, Ti, Fe, Mg, Ba, Zn, germanium, and Nb) which replaced a part of Mn by other metal ions, and Li_{[Lix Mn_{2-x}] O₄} which were replaced by the lithium ion It was tried. And LiCr_x Mn_{2-x} O₄ The increase of the stability of the mother structure of a spinel and the cycle property improved.

[0005] However, the further improvement was called for. Therefore, the technical problem which this invention tends to solve is offering the lithium secondary battery by which capacity degradation at the time of repeating a charge-and-discharge cycle was prevented.

[0006]

[Means for Solving the Problem] The technical problem of the aforementioned this invention is solved by the electrode which is constituted using the material replaced by boron and/or aluminum or boron and/or aluminum, and transition metals in some manganese of a spinel type lithium manganic acid ghost, and is characterized by the bird clapper.

[0007] The electrode which is constituted using the material especially expressed with Li_{Bx} M_y Mn_{2-x-y} O₄ (0 < x, 0 <= y, 0 < x+y < 1 and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind), and is characterized by the bird clapper is solved. Moreover, the electrode which is constituted using the material expressed with Li_{Alx} M_y Mn_{2-x-y} O₄ (0 < x, 0 <= y, 0 < x+y < 1 and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind), and is characterized by the bird clapper is solved.

[0008] In addition, the above-mentioned Li_{Bx} M_y Mn_{2-x-y} O₄ Li_{Alx} M_y Mn_{2-x-y} O₄ It sets and that [x] 0-1, and whose x+y are 0.01-1 is [0.01-1y] desirable. As for especially x, 0.05-0.2 are desirable. As for y, 0.05-0.2 are desirable. Moreover, the technical problem of the aforementioned this invention is solved by the lithium secondary battery characterized by the bird clapper from the positive electrode which consists of the above-mentioned electrode, a negative electrode, and the electrolytic solution.

[0009] In addition, the negative electrode in the above-mentioned lithium secondary battery consists of material chosen from the groups of an intercalation compound like for example, a lithium metal or carbon. Moreover, the electrolytic solution in the above-mentioned lithium secondary battery consists of nonaqueous electrolytes which dissolved lithium salt in the organic solvent. And since the electrode made to constitute as mentioned above is the thing of the structure by which atomic weight was small and replaced some manganese of a spinel type lithium manganic acid ghost from Mn with trivalent boron ion and trivalent aluminum ion with strong binding energy with oxygen, capacity degradation at the time of repeating a charge-and-discharge cycle is prevented effectively.

[0010]

[Embodiments of the Invention] The electrode of this invention, especially the positive electrode of a lithium secondary battery are constituted using the material replaced by boron and/or aluminum or boron and/or aluminum,

and transition metals in some manganese of a spinel type lithium manganic acid ghost. It is constituted using the material especially expressed with $\text{LiB}_x \text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ ($0 < x, 0 \leq y, 0 < x+y < 1$ and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind). Moreover, it is constituted using the material expressed with $\text{LiAl}_x \text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ ($0 < x, 0 \leq y, 0 < x+y < 1$ and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind). And x is [especially 0.01-1 (especially 0.05-0.2), and x+y of 0.01-1 (especially 0.05-0.2)y] 0.01-1.

[0011] Moreover, the lithium secondary battery of this invention consists of the positive electrode which consists of the above-mentioned electrode, a negative electrode, and the electrolytic solution. The negative electrode in this lithium secondary battery is chosen from the groups of an intercalation compound like for example, a lithium metal or carbon. Moreover, the electrolytic solution consists of nonaqueous electrolytes which dissolved lithium salt in the organic solvent. Hereafter, it explains further.

[0012] [LiB_x Mn_{2-x} O₄]

Manganese salt, or oxy-manganese hydroxide and manganic acid ghosts, such as lithium salt; manganese carbonate, such as a lithium carbonate and a lithium hydroxide, manganese acetate, oxalic acid manganese, manganese hydroxide, and manganese dioxide; weighing capacity of a boron salt or boron oxides, such as boric-acid and diacid-ized boron, is carried out so that it may be set to $\text{Li:B:Mn}=1:x:2-x$ (element ratio).

[0013] The raw material which carried out weighing capacity is fully mixed with an agate mortar. After mixture and in air or an oxygen air current, at 450 degrees C, it applies for 90 minutes and heat-treats. Then, an agate mortar grinds, and it calcinates over 24 hours again at 600-800 degrees C, and cools slowly, and is LiB_x Mn_{2-x} O₄. It obtained.

[LiB_x My Mn_{2-x-y} O₄ (M is Cr, Fe, Co, and nickel)]

Manganese salt, or oxy-manganese hydroxide and manganic acid ghosts, such as lithium salt; manganese carbonate, such as a lithium carbonate and a lithium hydroxide, manganese acetate, oxalic acid manganese, manganese hydroxide, and manganese dioxide; weighing capacity of the compounds, such as salts, such as boron salts, such as boric-acid and diacid-ized boron, or a carbonate of boron oxide; M (M is Cr, Fe, Co, and nickel), acetate, and an oxalate, an oxide, a hydroxide, or an oxy-hydroxide, is carried out so that it may become $\text{Li:B:M:Mn}=1:x:y$:

[0014] The raw material which carried out weighing capacity is fully mixed with an agate mortar. After mixture and in air or an oxygen air current, at 450 degrees C, it applies for 90 minutes and heat-treats. Then, the agate mortar ground, again, it calcinates and cooled slowly over 24 hours at 600-800 degrees C, and LiB_x My Mn_{2-x-y} O₄ (M is Cr, Fe, Co, and nickel) was obtained.

[0015] [LiAl_x Mn_{2-x} O₄]

Manganese salt, or oxy-manganese hydroxide and manganic acid ghosts, such as lithium salt; manganese carbonate, such as a lithium carbonate and a lithium hydroxide, manganese acetate, oxalic acid manganese, manganese hydroxide, and manganese dioxide; weighing capacity of the aluminium compounds, such as an aluminum hydroxide, is carried out so that it may be set to $\text{Li:aluminum:Mn}=1:x:2-x$ (element ratio).

[0016] The raw material which carried out weighing capacity is fully mixed with an agate mortar. After mixture and in air or an oxygen air current, at 450 degrees C, it applies for 90 minutes and heat-treats. Then, an agate mortar grinds, and it calcinates over 24 hours again at 600-800 degrees C, and cools slowly, and is LiAl_x Mn_{2-x} O₄. It obtained.

[LiAl_x My Mn_{2-x-y} O₄ (M is Cr, Fe, Co, and nickel)]

Manganese salt, or oxy-manganese hydroxide and manganic acid ghosts, such as lithium salt; manganese carbonate, such as a lithium carbonate and a lithium hydroxide, manganese acetate, oxalic acid manganese, manganese hydroxide, and manganese dioxide; weighing capacity of the compounds, such as salts, such as a carbonate of aluminium-compound; M (M is Cr, Fe, Co, and nickel), such as an aluminum hydroxide, acetate, and an oxalate, an oxide, a hydroxide, or an oxy-hydroxide, is carried out so that it may become $\text{Li:aluminum:M:Mn}=1:x:y:2-x-y$ (element ratio).

[0017] The raw material which carried out weighing capacity is fully mixed with an agate mortar. After mixture and in air or an oxygen air current, at 450 degrees C, it applies for 90 minutes and heat-treats. Then, the agate mortar ground, again, it calcinates and cooled slowly over 24 hours at 600-800 degrees C, and LiAl_x My Mn_{2-x-y} O₄ (M is Cr, Fe, Co, and nickel) was obtained.

[0018] Binders, such as current collection material, such as material obtained as mentioned above and acetylene black, and polytetrafluoroethylene, were kneaded with the agate mortar, and it rolled out in the shape of a film, it pierced circularly, and considered as the electrode pellet. And the lithium secondary battery was constituted using the electrolytic solution which consists of a positive electrode which consists of this electrode pellet, for example, the negative electrode which consists of an electrode which consisted of material chosen from the groups of an intercalation compound like a lithium metal or carbon, and a nonaqueous electrolyte which dissolved lithium salt in the organic solvent.

[0019]

[Example 1] As the form of implementation of the above-mentioned invention explained, it is LiB₁ / 6 Mn₁₁ / 6O₄.

It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of the lithium perchlorate of 1 mol/l, and these constituted the lithium secondary battery.

[0020]

[Example 2] As the form of implementation of the above-mentioned invention explained, it is LiAl1 / 6 Mn11 / 6O4. It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of the lithium perchlorate of 1 mol/l, and these constituted the lithium secondary battery.

[0021] And current density 0.2 mA/cm² Since the charge and discharge test was performed in the potential range of 4.5v to 3.5v and change of the capacity density at the time of electric discharge was investigated, the result is shown in drawing 2.

[0022]

[Example 3] As the form of implementation of the above-mentioned invention explained, LiB1/12Cr1 / 12Mn11 / 6O4 was obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [1.] lithium perchlorate, and these constituted the lithium secondary battery.

[0023] And current density 0.2 mA/cm² Since the charge and discharge test was performed in the potential range of 4.5v to 3.5v and change of the capacity density at the time of electric discharge was investigated, the result is shown in drawing 3.

[0024]

[Example 4] As the form of implementation of the above-mentioned invention explained, LiB1/12Fe1 / 12Mn11 / 6O4 was obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [1.] lithium perchlorate, and these constituted the lithium secondary battery.

[0025]

[Example 5] As the form of implementation of the above-mentioned invention explained, LiB1/12Co1 / 12Mn11 / 6O4 was obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [1.] lithium perchlorate, and these constituted the lithium secondary battery.

[0026]

[Example 6] As the form of implementation of the above-mentioned invention explained, LiB1/12nickel1 / 12Mn11 / 6O4 was obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [1.] lithium perchlorate, and these constituted the lithium secondary battery.

[0027]

[Example 7] As the form of implementation of the above-mentioned invention explained, it is LiAl1/12Cr1 / 12Mn11 / 6O4. It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [1.] lithium perchlorate, and these constituted the lithium secondary battery.

[0028]

[Example 8] As the form of implementation of the above-mentioned invention explained, it is LiAl1/12Fe1 / 12Mn11 / 6O4. It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [1.] lithium perchlorate, and these constituted the lithium secondary battery.

[0029]

[Example 9] As the form of implementation of the above-mentioned invention explained, it is LiAl1/12Co1 / 12Mn11 / 6O4. It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [1.] lithium perchlorate, and these constituted the lithium secondary battery.

[0030]

[Example 10] As the form of implementation of the above-mentioned invention explained, it is LiAl1/12nickel1 / 12Mn11 / 6O4. It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [1.] lithium perchlorate, and these constituted the lithium secondary battery.

[0031]

[Property] About the lithium secondary battery of each above-mentioned example, it is current density 0.2 mA/cm². Since the charge and discharge test was performed in the potential range of 4.5v to 3.5v and change of the capacity density at the time of electric discharge was investigated, some are shown in drawing 1 (example 1), drawing 2

(example 2), and drawing 3 (example 3).

[0032] According to this, it turns out that capacity degradation at the time of repeating a charge-and-discharge cycle is prevented. Especially Some manganese of a spinel type lithium manganic acid ghost Material $\text{LiB}_x \text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ ($0 < x, 0 < y, 0 < x+y < 1$ and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind) and LiAl_x which were replaced by boron and/or aluminum, and transition metals The thing of the electrode which it comes to constitute using the material expressed with $\text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ ($0 < x, 0 < y, 0 < x+y < 1$ and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind) It turns out that capacity degradation at the time of repeating a charge-and-discharge cycle is prevented.

[0033]

[Effect of the Invention] Capacity degradation at the time of repeating a charge-and-discharge cycle is prevented.

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[0004] In order to improve capacity degradation by the repeat of this charge-and-discharge cycle, it is LiMn₂O₄. Li_{[Mx Mn_{2-x}] O₄} (M is Cr, Co, nickel, Ti, Fe, Mg, Ba, Zn, germanium, and Nb) which replaced a part of Mn by other metal ions, and Li_{[Lix Mn_{2-x}] O₄} which were replaced by the lithium ion It was tried. And LiCr_x Mn_{2-x} O₄ The increase of the stability of the mother structure of a spinel and the cycle property improved.

[0005] However, the further improvement was called for. Therefore, the technical problem which this invention tends to solve is offering the lithium secondary battery by which capacity degradation at the time of repeating a charge-and-discharge cycle was prevented.

[0006]

[Means for Solving the Problem] The technical problem of the aforementioned this invention is solved by the electrode which is constituted using the material replaced by boron and/or aluminum or boron and/or aluminum, and transition metals in some manganese of a spinel type lithium manganic acid ghost, and is characterized by the bird clapper.

[0007] The electrode which is constituted using the material especially expressed with LiB_x M_y Mn_{2-x-y} O₄ (0 < x, 0 <= y, 0 < x+y < 1 and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind), and is characterized by the bird clapper is solved. Moreover, the electrode which is constituted using the material expressed with LiAl_x M_y Mn_{2-x-y} O₄ (0 < x, 0 <= y, 0 < x+y < 1 and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind), and is characterized by the bird clapper is solved.

[0008] In addition, the above-mentioned LiB_x M_y Mn_{2-x-y} O₄ LiAl_x M_y Mn_{2-x-y} O₄ It sets and that [x] 0-1, and whose x+y are 0.01-1 is [0.01-1y] desirable. As for especially x, 0.05-0.2 are desirable. As for y, 0.05-0.2 are desirable. Moreover, the technical problem of the aforementioned this invention is solved by the lithium secondary battery characterized by the bird clapper from the positive electrode which consists of the above-mentioned electrode, a negative electrode, and the electrolytic solution.

[0009] In addition, the negative electrode in the above-mentioned lithium secondary battery consists of material chosen from the groups of an intercalation compound like for example, a lithium metal or carbon. Moreover, the electrolytic solution in the above-mentioned lithium secondary battery consists of nonaqueous electrolytes which dissolved lithium salt in the organic solvent. And since the electrode made to constitute as mentioned above is the thing of the structure by which atomic weight was small and replaced some manganese of a spinel type lithium manganic acid ghost from Mn with trivalent boron ion and trivalent aluminum ion with strong binding energy with oxygen, capacity degradation at the time of repeating a charge-and-discharge cycle is prevented effectively.

[0010]

[Embodiments of the Invention] The electrode of this invention, especially the positive electrode of a lithium secondary battery are constituted using the material replaced by boron and/or aluminum or boron and/or aluminum,

and transition metals in some manganese of a spinel type lithium manganic acid ghost. It is constituted using the material especially expressed with $\text{LiB}_x \text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ ($0 < x, 0 \leq y, 0 < x+y < 1$ and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind). Moreover, it is constituted using the material expressed with $\text{LiAl}_x \text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ ($0 < x, 0 \leq y, 0 < x+y < 1$ and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind). And x is [especially 0.01-1 (especially 0.05-0.2), and x+y of 0.01-1 (especially 0.05-0.2)y] 0.01-1.

[0011] Moreover, the lithium secondary battery of this invention consists of the positive electrode which consists of the above-mentioned electrode, a negative electrode, and the electrolytic solution. The negative electrode in this lithium secondary battery is chosen from the groups of an intercalation compound like for example, a lithium metal or carbon. Moreover, the electrolytic solution consists of nonaqueous electrolytes which dissolved lithium salt in the organic solvent. Hereafter, it explains further.

[0012] [$\text{LiB}_x \text{Mn}_{2-x} \text{O}_4$]

Manganese salt, or oxy-manganese hydroxide and manganic acid ghosts, such as lithium salt; manganese carbonate, such as a lithium carbonate and a lithium hydroxide, manganese acetate, oxalic acid manganese, manganese hydroxide, and manganese dioxide; weighing capacity of a boron salt or boron oxides, such as boric-acid and diacid-ized boron, is carried out so that it may be set to $\text{Li:B:Mn}=1:x:2-x$ (element ratio).

[0013] The raw material which carried out weighing capacity is fully mixed with an agate mortar. After mixture and in air or an oxygen air current, at 450 degrees C, it applies for 90 minutes and heat-treats. Then, an agate mortar grinds, and it calcinates over 24 hours again at 600-800 degrees C, and cools slowly, and is $\text{LiB}_x \text{Mn}_{2-x} \text{O}_4$. It obtained.

[$\text{LiB}_x \text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ (M is Cr, Fe, Co, and nickel)]

Manganese salt, or oxy-manganese hydroxide and manganic acid ghosts, such as lithium salt; manganese carbonate, such as a lithium carbonate and a lithium hydroxide, manganese acetate, oxalic acid manganese, manganese hydroxide, and manganese dioxide; weighing capacity of the compounds, such as salts, such as boron salts, such as boric-acid and diacid-ized boron, or a carbonate of boron oxide; M (M is Cr, Fe, Co, and nickel), acetate, and an oxalate, an oxide, a hydroxide, or an oxy-hydroxide, is carried out so that it may become $\text{Li:B:M:Mn}=1:x:y$:

[0014] The raw material which carried out weighing capacity is fully mixed with an agate mortar. After mixture and in air or an oxygen air current, at 450 degrees C, it applies for 90 minutes and heat-treats. Then, the agate mortar ground, again, it calcinates and cooled slowly over 24 hours at 600-800 degrees C, and $\text{LiB}_x \text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ (M is Cr, Fe, Co, and nickel) was obtained.

[0015] [$\text{LiAl}_x \text{Mn}_{2-x} \text{O}_4$]

Manganese salt, or oxy-manganese hydroxide and manganic acid ghosts, such as lithium salt; manganese carbonate, such as a lithium carbonate and a lithium hydroxide, manganese acetate, oxalic acid manganese, manganese hydroxide, and manganese dioxide; weighing capacity of the aluminium compounds, such as an aluminum hydroxide, is carried out so that it may be set to $\text{Li:aluminum:Mn}=1:x:2-x$ (element ratio).

[0016] The raw material which carried out weighing capacity is fully mixed with an agate mortar. After mixture and in air or an oxygen air current, at 450 degrees C, it applies for 90 minutes and heat-treats. Then, an agate mortar grinds, and it calcinates over 24 hours again at 600-800 degrees C, and cools slowly, and is $\text{LiAl}_x \text{Mn}_{2-x} \text{O}_4$. It obtained.

[$\text{LiAl}_x \text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ (M is Cr, Fe, Co, and nickel)]

Manganese salt, or oxy-manganese hydroxide and manganic acid ghosts, such as lithium salt; manganese carbonate, such as a lithium carbonate and a lithium hydroxide, manganese acetate, oxalic acid manganese, manganese hydroxide, and manganese dioxide; weighing capacity of the compounds, such as salts, such as a carbonate of aluminium-compound; M (M is Cr, Fe, Co, and nickel), such as an aluminum hydroxide, acetate, and an oxalate, an oxide, a hydroxide, or an oxy-hydroxide, is carried out so that it may become $\text{Li:aluminum:M:Mn}=1:x:y:2-x-y$ (element ratio).

[0017] The raw material which carried out weighing capacity is fully mixed with an agate mortar. After mixture and in air or an oxygen air current, at 450 degrees C, it applies for 90 minutes and heat-treats. Then, the agate mortar ground, again, it calcinates and cooled slowly over 24 hours at 600-800 degrees C, and $\text{LiAl}_x \text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ (M is Cr, Fe, Co, and nickel) was obtained.

[0018] Binders, such as current collection material, such as material obtained as mentioned above and acetylene black, and polytetrafluoroethylene, were kneaded with the agate mortar, and it rolled out in the shape of a film, it pierced circularly, and considered as the electrode pellet. And the lithium secondary battery was constituted using the electrolytic solution which consists of a positive electrode which consists of this electrode pellet, for example, the negative electrode which consists of an electrode which consisted of material chosen from the groups of an intercalation compound like a lithium metal or carbon, and a nonaqueous electrolyte which dissolved lithium salt in the organic solvent.

[0019]

[Example 1] As the form of implementation of the above-mentioned invention explained, it is $\text{LiB}_1/6 \text{Mn}_{11}/6\text{O}_4$.

It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of the lithium perchlorate of 1 mol/l, and these constituted the lithium secondary battery.

[0020]

[Example 2] As the form of implementation of the above-mentioned invention explained, it is LiAl1 / 6 Mn11 / 6O4. It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of the lithium perchlorate of 1 mol/l, and these constituted the lithium secondary battery.

[0021] And current density 0.2 mA/cm² Since the charge and discharge test was performed in the potential range of 4.5v to 3.5v and change of the capacity density at the time of electric discharge was investigated, the result is shown in drawing 2.

[0022]

[Example 3] As the form of implementation of the above-mentioned invention explained, LiB1/12Cr1 / 12Mn11 / 6O4 was obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [l.] lithium perchlorate, and these constituted the lithium secondary battery.

[0023] And current density 0.2 mA/cm² Since the charge and discharge test was performed in the potential range of 4.5v to 3.5v and change of the capacity density at the time of electric discharge was investigated, the result is shown in drawing 3.

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[0025]

[Example 5] As the form of implementation of the above-mentioned invention explained, LiB1/12Co1 / 12Mn11 / 6O4 was obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [l.] lithium perchlorate, and these constituted the lithium secondary battery.

[0026]

[Example 6] As the form of implementation of the above-mentioned invention explained, LiB1/12nickel1 / 12Mn11 / 6O4 was obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [l.] lithium perchlorate, and these constituted the lithium secondary battery.

[0027]

[Example 7] As the form of implementation of the above-mentioned invention explained, it is LiAl1/12Cr1 / 12Mn11 / 6O4. It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [l.] lithium perchlorate, and these constituted the lithium secondary battery.

[0028]

[Example 8] As the form of implementation of the above-mentioned invention explained, it is LiAl1/12Fe1 / 12Mn11 / 6O4. It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [l.] lithium perchlorate, and these constituted the lithium secondary battery.

[0029]

[Example 9] As the form of implementation of the above-mentioned invention explained, it is LiAl1/12Co1 / 12Mn11 / 6O4. It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [l.] lithium perchlorate, and these constituted the lithium secondary battery.

[0030]

[Example 10] As the form of implementation of the above-mentioned invention explained, it is LiAl1/12nickel1 / 12Mn11 / 6O4. It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [l.] lithium perchlorate, and these constituted the lithium secondary battery.

[0031]

[Property] About the lithium secondary battery of each above-mentioned example, it is current density 0.2 mA/cm². Since the charge and discharge test was performed in the potential range of 4.5v to 3.5v and change of the capacity density at the time of electric discharge was investigated, some are shown in drawing 1 (example 1), drawing 2

(example 2), and drawing 3 (example 3).

[0032] According to this, it turns out that capacity degradation at the time of repeating a charge-and-discharge cycle is prevented. Especially Some manganese of a spinel type lithium manganic acid ghost Material $\text{LiB}_x \text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ ($0 < x, 0 < y, 0 < x+y < 1$ and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind) and LiAl_x which were replaced by boron and/or aluminum, and transition metals The thing of the electrode which it comes to constitute using the material expressed with $\text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ ($0 < x, 0 < y, 0 < x+y < 1$ and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind) It turns out that capacity degradation at the time of repeating a charge-and-discharge cycle is prevented.

[0033]

[Effect of the Invention] Capacity degradation at the time of repeating a charge-and-discharge cycle is prevented.

[Translation done.]

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to a lithium secondary battery.

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EFFECT OF THE INVENTION

[Effect of the Invention] Capacity degradation at the time of repeating a charge-and-discharge cycle is prevented.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] It is LiMn₂O₄ by Thackeray and others. Since the possibility as a positive-electrode material for lithium secondary batteries which shows the high potential called 4v was suggested, many researchers have inquired briskly. However, LiMn₂O₄ The lithium secondary battery used as a positive electrode has the fault to which capacity falls gradually, when charge and discharge are repeated.

[0003] Namely, LiMn₂O₄ If a shell Li is made to break away, crookedness of potential will occur [lithium composition] in the 1/2 neighborhood, and grid volume will contract greatly simultaneously. On the contrary, if lithium composition inserts a lithium and goes from a small field, expansion of grid volume will occur [lithium composition] in the 1/2 neighborhood. Thus, the phase transition accompanied by expansion and contraction of grid volume happens at the time of charge and discharge, and it is considered the cause of capacity degradation at the time of this repeating a charge-and-discharge cycle.

[0004] In order to improve capacity degradation by the repeat of this charge-and-discharge cycle, it is LiMn₂O₄. Li[M_xMn_{2-x}]O₄ (M is Cr, Co, nickel, Ti, Fe, Mg, Ba, Zn, germanium, and Nb) which replaced a part of Mn by other metal ions, and Li[LixMn_{2-x}]O₄ which were replaced by the lithium ion It was tried. And LiCr_xMn_{2-x}O₄ The increase of the stability of the mother structure of a spinel and the cycle property improved.

[0005] However, the further improvement was called for. Therefore, the technical problem which this invention tends to solve is offering the lithium secondary battery by which capacity degradation at the time of repeating a charge-and-discharge cycle was prevented.

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MEANS

[Means for Solving the Problem] The technical problem of the aforementioned this invention is solved by the electrode which is constituted using the material replaced by boron and/or aluminum or boron and/or aluminum, and transition metals in some manganese of a spinel type lithium manganic acid ghost, and is characterized by the bird clapper.

[0007] The electrode which is constituted using the material especially expressed with $\text{LiB}_x \text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ ($0 < x, 0 \leq y, 0 < x+y < 1$ and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind), and is characterized by the bird clapper is solved. Moreover, the electrode which is constituted using the material expressed with $\text{LiAl}_x \text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ ($0 < x, 0 \leq y, 0 < x+y < 1$ and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind), and is characterized by the bird clapper is solved.

[0008] In addition, the above-mentioned $\text{LiB}_x \text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ $\text{LiAl}_x \text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ It sets and that [x] 0-1, and whose $x+y$ are 0.01-1 is [0.01-1y] desirable. As for especially x, 0.05-0.2 are desirable. As for y, 0.05-0.2 are desirable. Moreover, the technical problem of the aforementioned this invention is solved by the lithium secondary battery characterized by the bird clapper from the positive electrode which consists of the above-mentioned electrode, a negative electrode, and the electrolytic solution.

[0009] In addition, the negative electrode in the above-mentioned lithium secondary battery consists of material chosen from the groups of an intercalation compound like for example, a lithium metal or carbon. Moreover, the electrolytic solution in the above-mentioned lithium secondary battery consists of nonaqueous electrolytes which dissolved lithium salt in the organic solvent. And since the electrode made to constitute as mentioned above is the thing of the structure by which atomic weight was small and replaced some manganese of a spinel type lithium manganic acid ghost from Mn with trivalent boron ion and trivalent aluminum ion with strong binding energy with oxygen, capacity degradation at the time of repeating a charge-and-discharge cycle is prevented effectively.

[0010]

[Embodiments of the Invention] The electrode of this invention, especially the positive electrode of a lithium secondary battery are constituted using the material replaced by boron and/or aluminum or boron and/or aluminum, and transition metals in some manganese of a spinel type lithium manganic acid ghost. It is constituted using the material especially expressed with $\text{LiB}_x \text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ ($0 < x, 0 \leq y, 0 < x+y < 1$ and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind). Moreover, it is constituted using the material expressed with $\text{LiAl}_x \text{M}_y \text{Mn}_{2-x-y} \text{O}_4$ ($0 < x, 0 \leq y, 0 < x+y < 1$ and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind). And x is [especially 0.01-1 (especially 0.05-0.2), and x+y of 0.01-1 (especially 0.05-0.2)y] 0.01-1.

[0011] Moreover, the lithium secondary battery of this invention consists of the positive electrode which consists of the above-mentioned electrode, a negative electrode, and the electrolytic solution. The negative electrode in this lithium secondary battery is chosen from the groups of an intercalation compound like for example, a lithium metal or carbon. Moreover, the electrolytic solution consists of nonaqueous electrolytes which dissolved lithium salt in the organic solvent. Hereafter, it explains further.

[0012] $[\text{LiB}_x \text{Mn}_{2-x} \text{O}_4]$

Manganese salt, or oxy-manganese hydroxide and manganic acid ghosts, such as lithium salt; manganese carbonate, such as a lithium carbonate and a lithium hydroxide, manganese acetate, oxalic acid manganese, manganese hydroxide, and manganese dioxide; weighing capacity of a boron salt or boron oxides, such as boric-acid and diacid-ized boron, is carried out so that it may be set to $\text{Li:B:Mn}=1:x:2-x$ (element ratio).

[0013] The raw material which carried out weighing capacity is fully mixed with an agate mortar. After mixture and in air or an oxygen air current, at 450 degrees C, it applies for 90 minutes and heat-treats. Then, an agate mortar grinds, and it calcinates over 24 hours again at 600-800 degrees C, and cools slowly, and is $\text{LiB}_x \text{Mn}_{2-x} \text{O}_4$. It obtained.

$[\text{LiB}_x \text{M}_y \text{Mn}_{2-x-y} \text{O}_4 \text{ (M is Cr, Fe, Co, and nickel)}]$

Manganese salt, or oxy-manganese hydroxide and manganic acid ghosts, such as lithium salt; manganese carbonate, such as a lithium carbonate and a lithium hydroxide, manganese acetate, oxalic acid manganese, manganese

hydroxide, and manganese dioxide; weighing capacity of the compounds, such as salts, such as boron salts, such as boric-acid and diacid-ized boron, or a carbonate of boron oxide; M (M is Cr, Fe, Co, and nickel), acetate, and an oxalate, an oxide, a hydroxide, or an oxy-hydroxide, is carried out so that it may become $Li:B:M:Mn=1:x:y$:
 [0014] The raw material which carried out weighing capacity is fully mixed with an agate mortar. After mixture and in air or an oxygen air current, at 450 degrees C, it applies for 90 minutes and heat-treats. Then, the agate mortar ground, again, it calcinated and cooled slowly over 24 hours at 600-800 degrees C, and $LiB_x My Mn_{2-x-y} O_4$ (M is Cr, Fe, Co, and nickel) was obtained.

[0015] $[LiAl_x Mn_{2-x} O_4]$

Manganese salt, or oxy-manganese hydroxide and manganic acid ghosts, such as lithium salt; manganese carbonate, such as a lithium carbonate and a lithium hydroxide, manganese acetate, oxalic acid manganese, manganese hydroxide, and manganese dioxide; weighing capacity of the aluminium compounds, such as an aluminum hydroxide, is carried out so that it may be set to $Li:aluminum:Mn=1:x:2-x$ (element ratio).

[0016] The raw material which carried out weighing capacity is fully mixed with an agate mortar. After mixture and in air or an oxygen air current, at 450 degrees C, it applies for 90 minutes and heat-treats. Then, an agate mortar grinds, and it calcinates over 24 hours again at 600-800 degrees C, and cools slowly, and is $LiAl_x Mn_{2-x} O_4$. It obtained.

[$LiAl_x My Mn_{2-x-y} O_4$ (M is Cr, Fe, Co, and nickel)]

Manganese salt, or oxy-manganese hydroxide and manganic acid ghosts, such as lithium salt; manganese carbonate, such as a lithium carbonate and a lithium hydroxide, manganese acetate, oxalic acid manganese, manganese hydroxide, and manganese dioxide; weighing capacity of the compounds, such as salts, such as a carbonate of aluminium-compound; M (M is Cr, Fe, Co, and nickel), such as an aluminum hydroxide, acetate, and an oxalate, an oxide, a hydroxide, or an oxy-hydroxide, is carried out so that it may become $Li:aluminum:M:Mn=1:x:y:2-x-y$ (element ratio).

[0017] The raw material which carried out weighing capacity is fully mixed with an agate mortar. After mixture and in air or an oxygen air current, at 450 degrees C, it applies for 90 minutes and heat-treats. Then, the agate mortar ground, again, it calcinated and cooled slowly over 24 hours at 600-800 degrees C, and $LiAl_x My Mn_{2-x-y} O_4$ (M is Cr, Fe, Co, and nickel) was obtained.

[0018] Binders, such as current collection material, such as material obtained as mentioned above and acetylene black, and polytetrafluoroethylene, were kneaded with the agate mortar, and it rolled out in the shape of a film, it pierced circularly, and considered as the electrode pellet. And the lithium secondary battery was constituted using the electrolytic solution which consists of a positive electrode which consists of this electrode pellet, for example, the negative electrode which consists of an electrode which consisted of material chosen from the groups of an intercalation compound like a lithium metal or carbon, and a nonaqueous electrolyte which dissolved lithium salt in the organic solvent.

[0019]

[Example 1] As the gestalt of implementation of the above-mentioned invention explained, it is $LiB_1 / 6 Mn_{11} / 6O_4$. It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of the lithium perchlorate of 1 mol/l, and these constituted the lithium secondary battery.

[0020]

[Example 2] As the gestalt of implementation of the above-mentioned invention explained, it is $LiAl_1 / 6 Mn_{11} / 6O_4$. It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of the lithium perchlorate of 1 mol/l, and these constituted the lithium secondary battery.

[0021] And current density 0.2 mA/cm² Since the charge and discharge test was performed in the potential range of 4.5v to 3.5v and change of the capacity density at the time of electric discharge was investigated, the result is shown in drawing 2 .

[0022]

[Example 3] As the gestalt of implementation of the above-mentioned invention explained, $LiB_{12}Cr_1 / 12Mn_{11} / 6O_4$ was obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [l.] lithium perchlorate, and these constituted the lithium secondary battery.

[0023] And current density 0.2 mA/cm² Since the charge and discharge test was performed in the potential range of 4.5v to 3.5v and change of the capacity density at the time of electric discharge was investigated, the result is shown in drawing 3 .

[0024]

[Example 4] As the gestalt of implementation of the above-mentioned invention explained, $LiB_{12}Fe_1 / 12Mn_{11} / 6O_4$ was obtained, the positive electrode was constituted using this, the negative electrode was constituted using the

metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [1.] lithium perchlorate, and these constituted the lithium secondary battery.

[0025]

[Example 5] As the gestalt of implementation of the above-mentioned invention explained, LiB1/12Co1 / 12Mn11 / 6O4 was obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [1.] lithium perchlorate, and these constituted the lithium secondary battery.

[0026]

[Example 6] As the gestalt of implementation of the above-mentioned invention explained, LiB1/12nickel1 / 12Mn11 / 6O4 was obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [1.] lithium perchlorate, and these constituted the lithium secondary battery.

[0027]

[Example 7] As the gestalt of implementation of the above-mentioned invention explained, it is LiAl1/12Cr1 / 12Mn11 / 6O4. It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [1.] lithium perchlorate, and these constituted the lithium secondary battery.

[0028]

[Example 8] As the gestalt of implementation of the above-mentioned invention explained, it is LiAl1/12Fe1 / 12Mn11 / 6O4. It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [1.] lithium perchlorate, and these constituted the lithium secondary battery.

[0029]

[Example 9] As the gestalt of implementation of the above-mentioned invention explained, it is LiAl1/12Co1 / 12Mn11 / 6O4. It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [1.] lithium perchlorate, and these constituted the lithium secondary battery.

[0030]

[Example 10] As the gestalt of implementation of the above-mentioned invention explained, it is LiAl1/12nickel1 / 12Mn11 / 6O4. It obtained, the positive electrode was constituted using this, the negative electrode was constituted using the metal lithium, the electrolytic solution was constituted from a propylene-carbonate solution of a 1 mol [1.] lithium perchlorate, and these constituted the lithium secondary battery.

[0031]

[Property] About the lithium secondary battery of each above-mentioned example, it is current density 0.2 mA/cm². Since the charge and discharge test was performed in the potential range of 4.5v to 3.5v and change of the capacity density at the time of electric discharge was investigated, some are shown in drawing 1 (example 1), drawing 2 (example 2), and drawing 3 (example 3).

[0032] According to this, it turns out that capacity degradation at the time of repeating a charge-and-discharge cycle is prevented. Especially Some manganese of a spinel type lithium manganic acid ghost Material LiB_x M_y Mn_{2-x-y} O₄ (0< x, 0< y, 0< x+y< 1 and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind) and LiAl_x which were replaced by boron and/or aluminum, and transition metals The thing of the electrode which it comes to constitute using the material expressed with M_y Mn_{2-x-y} O₄ (0< x, 0< y, 0< x+y< 1 and M are chosen from the groups of Cr, Fe, Co, and nickel at least a kind) It turns out that capacity degradation at the time of repeating a charge-and-discharge cycle is prevented.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The graph which shows change of the capacity density at the time of electric discharge of the lithium secondary battery of an example 1

[Drawing 2] The graph which shows change of the capacity density at the time of electric discharge of the lithium secondary battery of an example 2

[Drawing 3] The graph which shows change of the capacity density at the time of electric discharge of the lithium secondary battery of an example 3

[Translation done.]

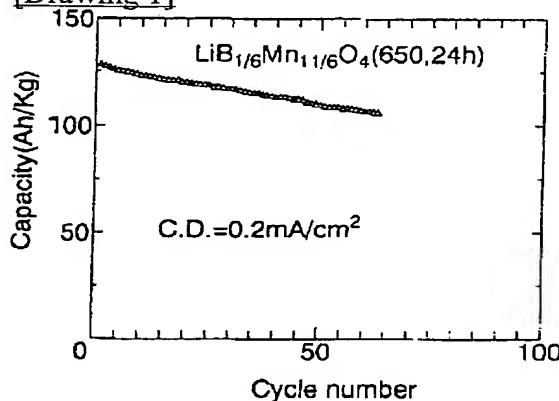
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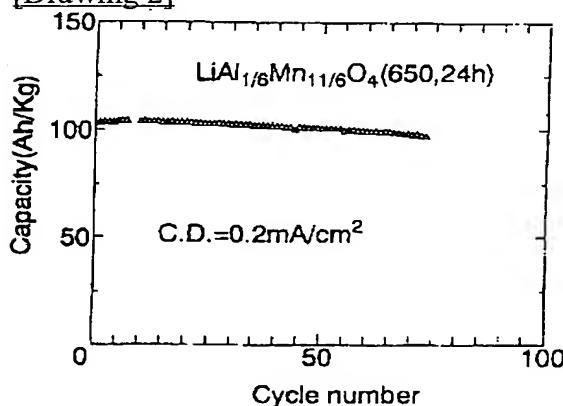
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DRAWINGS

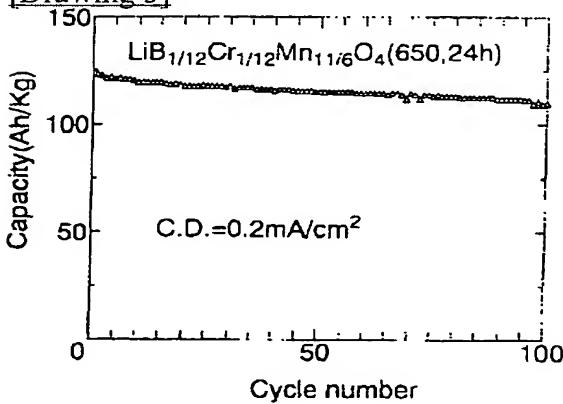
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]